



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

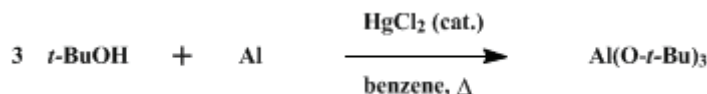
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.48 (1955); Vol. 21, p.8 (1941).

ALUMINUM *tert*-BUTOXIDE



Submitted by Winston Wayne and Homer Adkins.

Checked by Nathan L. Drake, Wm. H. Souder, Jr., and Ralph Mozingo.

1. Procedure

In a 2-l. round-bottomed flask, bearing a reflux condenser protected by a calcium chloride tube, are placed 64 g. (2.37 gram atoms) of **aluminum** shavings, 200 g. (254 ml., 2.7 moles) of dry *tert*-butyl alcohol, and 5–10 g. of **aluminum *tert*-butoxide** (Note 1). After the mixture is heated to boiling on a steam bath, approximately 0.4 g. of **mercuric chloride** is added followed by vigorous shaking (Note 2). As the heating is continued the color of the reaction mixture gradually changes from clear to milky to black, and **hydrogen** is evolved. When the mixture has become black, the heating is interrupted.

After the reaction has been allowed to proceed for an hour without heating, an additional 244 g. (309 ml., 3.3 moles) of dry *tert*-butyl alcohol (total quantity, 6 moles) and 200 ml. of dry **benzene** are added. The reaction will again set in upon gentle heating and will continue vigorously without further heating. After about 2 hours the reaction subsides and the mixture is refluxed for about 10 hours.

The **benzene** and unchanged *tert*-butyl alcohol are removed by distillation from the steam bath, the final traces being removed under 10–30 mm. pressure. A liter of dry **ether** is added, and the solid **aluminum *tert*-butoxide** is dissolved by refluxing for a short period. After cooling, 35 ml. of **undried ether** is added, followed immediately by vigorous shaking (Note 3). After standing for 2 hours the solution is centrifuged for 30 minutes to remove unused **aluminum**, **aluminum hydroxide**, and **mercury** (Note 4).

The solvent is removed by distillation from the steam bath, the final traces under 10–30 mm. pressure. The flask is allowed to cool with a calcium chloride tube attached, and the product is crushed with a spatula and transferred to bottles sealed against moisture. The yield is 394–418 g. (80–85%) of a white or slightly gray solid.

2. Notes

1. Commercial *tert*-butyl alcohol dried over **calcium oxide** is suitable for this preparation. **Aluminum isopropoxide** or **ethoxide**^{1,2} may be used in place of the **aluminum *tert*-butoxide** to remove traces of water. The grade of metal known as "fast cutting rods" has proved most satisfactory. The checkers used turnings made from **aluminum** cast from melted-down kitchen utensils. **Aluminum *tert*-butoxide** has also been prepared successfully in another laboratory from commercially pure **aluminum** (2S) and from rods of the alloy 17ST (communication from L. F. Fieser). The checkers were able to obtain considerably higher yields of the **butoxide** from pure **aluminum** than from a copper-bearing alloy.

2. The use of larger amounts of **mercuric chloride** increases the difficulty of getting the final product free from color. This difficulty may be avoided by previously amalgamating the **aluminum**.^{3,4} The mixture is shaken to distribute the **mercuric chloride** and thus aid in an even amalgamation of the **aluminum**.

3. The small amount of water introduced with the undried **ether** forms **aluminum hydroxide** which aids in the precipitation of the black suspended material. Shaking is essential to obtain the hydroxide formation throughout the solution.

4. The centrifuging may be carried out in 250-ml. stoppered bottles at 2000 r.p.m. After centrifuging, the solution should be colorless or light tan. If it is still dark in color another 25-ml. portion of undried **ether** should be added and the centrifuging repeated.

3. Discussion

Aluminum *tert*-butoxide can be prepared by refluxing dry *tert*-butyl alcohol with amalgamated aluminum^{1,5,6} or aluminum plus mercuric chloride.⁶ The method described is that of Adkins and Cox.⁶ The preparation of amalgamated aluminum has been described.^{3,4} Aluminum isopropoxide can be prepared from dry isopropyl alcohol and aluminum,^{1,2} the method being essentially that described for aluminum ethoxide.⁷

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 207
- Org. Syn. Coll. Vol. 3, 367

References and Notes

1. Tischtschenko, *J. Russ. Phys. Chem. Soc.*, **31**, 694 (1899) [*Chem. Zentr.*, **71**, I, 10 (1900)].
2. Young, Hartung, and Crossley, *J. Am. Chem. Soc.*, **58**, 100 (1936).
3. Wislicenus and Kaufman, *Ber.*, **28**, 1325 (1895).
4. Adkins, *J. Am. Chem. Soc.*, **44**, 2175 (1922).
5. Oppenauer, *Rec. trav. chim.*, **56**, 137 (1937).
6. Adkins and Cox, *J. Am. Chem. Soc.*, **60**, 1151 (1938).
7. *Org. Syntheses Coll. Vol. 2*, 599 (1943).

Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

copper-bearing

Benzene (71-43-2)

ether (60-29-7)

hydrogen (1333-74-0)

aluminum (7429-90-5)

mercury (7439-97-6)

isopropyl alcohol (67-63-0)

aluminum isopropoxide

mercuric chloride (7487-94-7)

calcium oxide

aluminum hydroxide

ethoxide

aluminum ethoxide

butoxide

tert-butyl alcohol (75-65-0)

ALUMINUM tert-BUTOXIDE